PATENT

Docket No. 297-056

Box Patent Application
Commissioner of Patents and Trademarks
Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): Ronald Redline, 28 Platt Drive, Prospect, CT. 06712
David Sawoska, 22 Kent Terrace, Watertown, CT. 06795
Peter Kukanskis, 245 Quassapaug Rd., Woodbury, CT. 06798

WARNING: *Patent must be applied for in the name(s) of all of the actual inventor(s). 37 CFR 1.41(a) and 1.53(b).*

For (title):

Method for Enhancing the Solderability of a Surface.

1. Type of Application

This new application is for a(n) (*check one applicable item below*):

- [x] Original
- [ ] Design
- [ ] Plant

WARNING: *Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4) unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

NOTE: If one of the following 3 items apply then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

- [ ] Divisional
- [ ] Continuation
- [ ] Continuation-in-part (CIP)

CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date Feb. 17, 1999 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EB 362988527 addressed to the: Commissioner of Patents and Trademarks, Washington, D.C. 20231.

John L. Cordani
(Type or print name of person mailing paper)


(Signature of person mailing paper)

NOTE. Each paper or fee referred to as enclosed herein has the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 CFR 1.10(b).

2. **Benefit of Prior U.S. Application(s) (35 USC 120)**

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

☐ The new application being transmitted claims the benefit of prior U.S. application(s) and enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

3. **Papers Enclosed Which Are Required For Filing Date Under 37 CFR 1.53(b) (Regular) or 37 CFR 1.153 (Design) Application**

15 Pages of specification

4 Pages of claims

1 Pages of Abstract

____ Sheets of drawing

☐ formal

☐ informal

WARNING: DO NOT submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. ***Only one copy is required or desired.*** *Comments on proposed new 37 CFR 1.84. Notice of March 9, 1988 (1990 O.G. 57-62).*

NOTE: "Identifying indicia such as the serial number, group and unit, title of the invention, attorney's docket number, inventor's name, number of sheets, etc., not to exceed 2¾ inches (7.0 cm.) in width may be placed in a centered location between the side edges within three fourths inch (19.1 mm.) of the top edge. Either this marking technique on the front of the drawing or the placement, although not preferred, of this information and the title of the invention on the back of the drawings is acceptable." Proposed 37 CFR 1.84(1). Notice of March 9, 1988 (1090 O.G. 57-62).

4. **Additional papers enclosed**

☐ Preliminary Amendment

☐ Information Disclosure Statement (37 CFR 1.98)

☐ Form PTO-1449

☐ Citations

☐ Declaration of Biological Deposit

☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.

☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative

☐ Special Comments

☐ Other

5. Declaration or oath

☒ Enclosed

executed by *(check all applicable boxes)*

☒ inventor(s).

☐ legal representative of inventor(s). 37 CFR 1.42 or 1.43

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

☐ this is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See item 13 below for fee.*

☐ Not Enclosed.

WARNING: Where the filing is a completion in the U.S. of an International Application but where a declaration is not available or where the completion of the U.S. application contains subject matter in addition to the International Application the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

☐ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of *all the above named inventor(s).* *(The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently)*

NOTE: It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).

☐ Showing that the filing is authorized. *(Not required unless called into question 37 CFR 1.41(d)*

6. Inventorship Statement

WARNING: If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted

The inventorship for all the claims in this application are:

☒ The same

or

☐ Are not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made.

☐ is submitted.

☐ will be submitted.

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. A verified English translation of the non-English language application and the processing fee of $130.00 required by 37 CFR 1.17(k) is required to be filed with the application or within such time as may be set by the Office. 37 CFR 1.52(d).

NOTE. A non-English oath or declaration in the form provided or approved by the PTO need not be translated. 37 CFR 1.69(b).

☒ English

☐ non-English

☐ the attached translation is a verified translation. 37 CFR 1.52(d).

8. Assignment

☒ An assignment of the invention to MacDermid, Incorporated
245 FReight St., Waterbury, CT. 06702

☒ is attached. A separate ☒ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☐ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters-one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

9. Certified Copy

Certified copy(ies) of application(s)

(country)	(appln. no.)	(filed)
(country)	(appln. no.)	(filed)
(country)	(appln. no.)	(filed)

from which priority is claimed

☐ is(are) attached.

☐ will follow.

NOTE The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. Fee Calculation (37 CFR 1.16)

A. ☒ Regular application

CLAIMS AS FILED

	Number filed		Number Extra		Rate	Basic Fee 37 CFR 1.16(a)
						$760.00
Total Claims (37 CFR 1.16(c))	20	−20=		X	$ 22.00	0.00
Independent Claims (37 CFR 1.16(b))	3	−3=		X	$ 74.00	0.00
Multiple dependent claim(s), if any (37 CFR 1.16(d))					$230.00	

☐ Amendment cancelling extra claims enclosed.

☐ Amendment deleting multiple-dependencies enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d)

Filing Fee Calculation $ 760.00

B. ☐ Design application
($290.00—37 CFR 1.16(f))

Filing Fee Calculation $_____

C. ☐ Plant application
($460.00—37 CFR 1.16(g))

Filing fee calculation $_____

11. Small Entity Statement(s)

☐ Verified Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is(are) attached.

Filing Fee Calculation (50% of A, B or C above) $_____

NOTE: Any excess of the full fee paid will be refunded if a verified statement and a refund request are filed within 2 months of the date of timely payment of a full fee. 37 CFR 1.28(a).

12. Request for International-Type Search (37 CFR 1.104(d)) ***(complete, if applicable)***

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made At This Time

☐ Not Enclosed

☐ No filing fee is to be paid at this time. (*This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently*)

☒ Enclosed

☒ basic filing fee $ 760.00

☒ recording assignment
($40.00; 37 CFR 1.21(h)) $ 40.00

☐ petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached. ($130.00; 37 CFR 1.47 and 1.17(h)) $_____

☐ for processing an application with a specification in a non-English language. ($130.00; 37 CFR 1.52(d) and 1.17(k) $_____

☐ processing and retention fee ($130.00; 37 CFR 1.53(d) and 1.21(l))

☐ fee for international-type search report ($40.00; 37 CFR 1.21(e)). $_____

NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application which is abandoned for failing to complete the application pursuant to 37 CFR 1.53(d) and this, as well as the changes to 37 CFR 1.53 and 1.78, indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid or the processing and retention fee of § 1.21(l) must be paid within 1 year from notification under § 53(d).

Total fees enclosed $800.00

14. Method of Payment of Fees

☒ Check in the amount of $800.00

☐ Charge Account No. _____ in the amount of $_____. A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

15. Authorization to Charge Additional Fees

WARNING: If no fees are to be paid on filing the following items should not be completed

WARNING: Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. _____:

☐ 37 CFR 1.16(a), (f) or (g) (filing fees)

☐ 37 CFR 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

☐ 37 CFR 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)

☐ 37 CFR 1.17 (application processing fees)

WARNING: While 37 CFR 1.17(a), (b), (c) and (d) deal with extensions of time under § 1.136(a) this authorization should be made only with the knowledge that, "Submission of the appropriate extension fee under 37 C.F.R 1.136(a) is to no avail unless a request or petition for extension is filed." (Emphasis added) Notice of November 5, 1985 (1060 O.G. 27)

☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . issue fee". From the wording of 37 CFR 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions As To Overpayment

☐ credit Account No. _____

☒ refund

Reg. No. 37,297

Tel. No. (203) 575-5646

SIGNATURE OF ATTORNEY

John L. Cordani

MacDermid, Incorporated

Type or print name of attorney

245 Freight Street

P.O. Address

Waterbury, CT. 06702

☐ **Incorporation by reference of added pages**

Check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED

☐ Plus Added Pages For New Application Transmittal Where Benefit Of Prior U.S. Application(s) Claimed

Number of pages added _____

☐ Plus Added Pages For Papers Referred To In Item 4 Above

Number of pages added _____

☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added _____

☒ **Statement Where No Further Pages Added**

(If no further pages form a part of this Transmittal then end this Transmittal with this page and check the following item)

☒ This transmittal ends with this page.

United States Patent Application

of

Ronald Redline
28 Platt Drive
Prospect, CT. 06712

and

David Sawoska
22 Kent Terrace
Watertown, CT. 06795

and

Peter Kukanskis
245 Quassapaug Road
Woodbury, CT. 06798

for

Method for Enhancing the Solderability of a Surface

Assigned To:
MacDermid, Incorporated
245 Freight Street
Waterbury, CT. 06702

John L. Cordani
Attorney for Applicant
Registration No. 37,297
MacDermid, Incorporated
245 Freight Street
Waterbury, CT. 06702
(203) 575-5646

METHOD FOR ENHANCING THE SOLDERABILITY OF A SURFACE

Field of the Invention

This invention relates generally to a method of treating a surface which treatment enhances the solderability of the surface. The method is particularly useful in the fabrication and assembly of printed circuit boards.

Background of the Invention

Soldering is generally used for making mechanical, electromechanical, or electronic connections to a variety of articles. The distinction between expected functions of the joints is important because each application has its own specific requirements for surface preparation. Of the three soldering applications, making electronic connections is the most demanding.

In the manufacture of electronic equipment utilizing printed circuits, connections of electronic components to the printed circuits are made by soldering of the leads of the components to the through-holes, surrounding pads, lands and other points of connection (collectively, "Areas of Connection"). Typically the connection occurs by wave soldering techniques.

To facilitate this soldering operation, the printed circuit fabricator is required to arrange that the through-holes, pads, lands and other points of connection are receptive to the subsequent soldering processes. Thus these surfaces must be readily wettable by the solder and permit an integral conductive connection with the leads or surfaces of the electronic components. Because

of these needs, printed circuit fabricators have devised various methods of preserving and enhancing the solderability of surfaces.

One means of arranging good solderability of the surfaces in question is to provide the surfaces with a pre-coating of solder. This is typically performed by a process called hot air solder leveling or through some type of plating process. In printed circuit fabrication, however, this method has several drawbacks. The use of hot air solder leveling may cause unacceptably high rate of defects due to shorts, particularly when dealing with small circuits. If plating is used, since it is not easy to selectively provide these areas with solder, all conductive areas of the board must be solder plated causing severe problems with the subsequent application of solder mask. In addition the foregoing processes are inefficient and relatively expensive.

Another means of arranging good solderability of these surfaces is to plate them with a final finish coating of a precious metal such as gold, palladium or rhodium. U.S. Patent No. 5,235,139 (Bengston, et. al.), the teachings of which are incorporated herein by reference, proposes a method for achieving this previous metal final finish. Bengston et. al. propose plating the copper areas to be soldered with electroless nickel-boron, followed by a precious metal coating such as gold. See also US Patent No. 4,940,181 to Juskey, Jr. et al., the teachings of which are incorporated herein by reference for a similar process which teaches the plating of electroless copper, followed by electrolytic copper, followed by nickel followed by gold as a solderable surface. These processes work well but are time consuming and expensive.

Various attempts have been made to selectively apply solder to the necessary areas only. One such method involves use of organic etch resists over the solder plated areas of connection followed by selective stripping of tin-lead from the copper traces before application of the solder mask. See US Patent No. 4,978,423 to Durnwith et. al. See also US Patent No. 5,160,579 to Larson, the teachings of which are incorporated herein by reference, for other known selective solder processes.

Soldering directly to copper surfaces has been difficult and inconsistent. These problems are due mainly to the inability of keeping the copper surfaces clean and free of oxidation throughout the soldering operation. Various organic treatments have been developed to preserve copper surfaces in a readily solderable state. For example, see US Patent No. 5,173,130 (Kinoshita) which teaches the use of certain 2-alkylbenzimidazoles as copper pre-fluxes to preserve the solderability of the copper surfaces. Treatments such as those taught in Kinoshita have proven successful but there is still need to improve the reliability of the process.

The method of preserving solderability proposed herein is the coating of copper surfaces to be soldered with an immersion silver plate prior to soldering. It has been found, however, that when the foregoing method is used the immersion silver coating has a tendency to develop outgrowths or filaments via an electromigration mechanism when the circuits are being used (ie. with voltage potentials present) in the presence of moisture.

The tendency for electromigration to occur can be measured by a standard technique specified in Bellcore GR-78-CORE (13.2.5, 13.2.7) standard test procedures which are incorporated herein by reference in their entirety. The foregoing Bellcore procedure measures the average insulation resistance between circuit features. Bellcore and IPC standards require, that the average insulation resistance not decrease by more than one decade between the initial value (obtained after a conditioning period of 96 hours at 85°C/85% relative humidity with no bias) and the final value (obtained after an additional 500 hours at 85°C/85% relative humidity with a 10 V.dc bias applied).

One method which may be used to overcome the electromigration of immersion silver plating is to coat the immersion silver plate with another more noble metal such as gold. The disadvantages of this method are the expense of gold plating as well as the necessity for additional process steps.

It is an object of this invention to propose a method for preserving and enhancing the solderability of copper surfaces by plating said copper surface with a novel immersion silver plate which is more resistant to electromigration than prior art immersion silver deposits.

Summary of the Invention

The current invention proposes the use of an immersion silver coating as an improved solderability preservative for various surfaces, particularly copper surfaces. Preferred

compositions for depositing the immersion silver coating are also disclosed. The novel immersion silver plating process produces a silver plate which is more resistant to electromigration than conventional immersion silver deposits. The process proposed is a versatile, low cost method for effectively preserving the solderability of surfaces, particularly copper surfaces and areas of connection on printed circuit boards.

Detailed Description of the Invention

The current invention proposes a process for preserving and enhancing the solderability of a metal surface, particularly copper surfaces. The proposed process comprises the following steps:

a). cleaning the metal surface;

b). optionally, etching the metal surface;

c). treating the metal surface with an immersion silver plating solution, said solution comprising:

1. a soluble source of silver ions;
2. an acid;
3. an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphoteric salts, resinous amines, resinous amides, fatty acids, resinous acids, and mixtures of the foregoing;
4. optionally, an imidazole, benzimidazole, or imidazole derivative; and
5. optionally, an oxidant.

Alternatively, the proposed process comprises the following steps:

a). cleaning the metal surfaces;

b). optionally, etching the metal surfaces;

c). treating the metal surface with an immersion silver plating solution;

d). treating the immersion silver plated surface with a solution which comprises an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphoteric salts, resinous amines, resinous amides, fatty acids, resinous acids and mixtures of the foregoing.

It has been discovered that immersion silver deposits provide excellent solderability preservatives, which are particularly useful in the fabrication of printed circuit boards. The solderability achievable with a simple immersion silver deposit in printed circuit applications has unexpectedly been found to exceed that achievable with prior art nickel-gold plating processes such as described in U.S. Patent No. 5,235,139 and unexpectedly exceeds that achievable with other immersion deposits. As can be seen in the examples to follow, the processes of the current invention yield surfaces which are very solderable under adverse conditions. In printed circuit applications the surfaces are wire bondable. In addition the incorporation of an additive, selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphoteric salts, resinous amines, resinous amides, fatty acids, resinous acids and mixtures of the foregoing, into the immersion silver deposit by incorporation in the plating bath or subsequent treatment of the plated surface greatly reduces the tendency of the silver deposit to electromigrate. Immersion plating is a process which results from a replacement reaction whereby the surface being plated dissolves into solution and at the same time the metal being plated deposits from the plating

solution onto the surface. The immersion plating initiates without prior activation of the surfaces. The metal to be plated is generally more noble than the surface metal. Thus immersion plating is usually significantly easier to control and significantly more cost effective than electroless plating, which requires sophisticated auto catalytic plating solutions and processes for activation of the surfaces prior to plating.

The soluble source of silver ions can be derived from a variety of silver compounds. The inventors have found silver nitrate to be most preferable. The concentration of silver in the plating solution can range from 0.1 to 25 grams per liter, but is most preferably present in a concentration of 0.5 to 2 grams per liter.

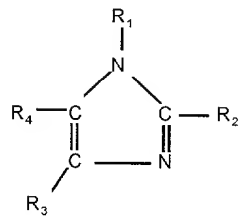
Although a variety of acids are suitable for use in this formulation, the inventors have found that methane sulfonic acid or nitric acid is most preferred. The concentration of acid in the plating solution can range from 1 to 150 grams per liter but is preferably in the range of 5 to 50 grams per liter.

In order to prevent or significantly reduce the tendency for immersion silver plates to electromigrate in the application proposed, the inventors have found it necessary to incorporate certain additives into the plated deposit, either by incorporation of the additives in the plating bath itself or by subsequent treatment of the plated surface with the additives. Incorporation of the additives into the plating bath itself is the preferred method. The additives may be selected from the group consisting of fatty amines, fatty acids, fatty amides, quaternary salts, amphoteric

salts, resinous amines, resinous amides, resinous acids and mixtures of the foregoing. Examples of suitable fatty amines are tallowamine and cocoamine. Examples of suitable fatty acids are stearic acid, oleic acid, palmitic acid and acids derived from the distillation of tall oil. Examples of suitable fatty amides are cocamide and tallowamide. Examples of suitable quaternary salts are (stearamidopropyl) dimethyl hydroxyethylammonium dihydrogen phosphate. Examples of suitable amphoteric salts are alkyliminodipropionic acid monosodium salts wherein the alkyl portion may be coco, tallow or similar organic alkyl chains. Examples of suitable resinous amines are amines derived from tall oil acids. Examples of suitable resinous amides are cocoamide, tallow amide and amides derived from tall oil acids. Examples of suitable resinous acids are acids derived from the distillation of tall oil such as abetic acid. Also suitable are ethoxylated and/or propoxylated versions of any of the foregoing materials such as ethoxylated or propoxylated fatty amines, ethoxylated or propoxylated fatty acids, ethoxylated or propoxylated quaternary salts, ethoxylated or propoxylated amphoteric salts, ethoxylated or propoxylated resinous amines, ethoxylated or propoxylated resinous amides, and ethoxylated or propoxylated resinous acids. Preferred additives include ethoxylated tallowamine, cyastat LS (quaternary ammonium methylsulfate of a fatty amidoalkyl amine) and ethoxylated cocoamine. The concentration of the foregoing additives in the immersion silver plating bath or in the subsequent surface treatment composition may range from 0.1 to 15 grams per liter but is preferably from 1 to 5 grams per liter.

The inventors have discovered that the inclusion of imidazole or imidazole derivative of the following formula has a significant positive impact upon the plate produced by immersion

plating solutions, particularly immersion silver plating solutions used in the processes of this invention:



Wherein R_1, R_2, R_3 and R_4 are independently selected from the group consisting of substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, halogens, nitro groups and hydrogen.

The inclusion of an imidazole as described above brightens the plated deposit and improves the integrity and physical properties of the resultant plated deposit. In addition, the imidazole also extends the useful life of the immersion plating solution. The inventors have found that histidine is a particularly preferred imidazole for the purposes of these processes.

The inclusion of imidazoles provides significant advantages in immersion plating solutions in general, but is particularly useful and advantageous in immersion silver plating. The inventors have found that immersion silver deposits resulting from plating baths containing imidazoles are brighter, smoother and more cohesive than immersion silver deposits plated from baths which do

not have imidazoles. In addition the immersion plating baths with imidazoles have longer effective lives than comparable baths without imidazoles. These same advantages are achievable by the inclusion of imidazoles in other immersion plating baths, including copper, palladium, gold, ruthenium and rhodium.

With respect to the immersion silver compositions useful in the present invention, the plating solution may, optionally, advantageously also contain an oxidant. The inventors have found that nitro aromatic compounds most preferably dinitro compounds, such as 3,5 dinitrohydroxybenzoic acid are preferred in this regard. The concentration of such an oxidant in the solution can range from 0.1 to 25 grams per liter, but is preferably from 0.5 to 2 grams per liter.

The immersion silver solution can be used in the processes of the current invention at temperatures ranging from room temperature to 200° F but is preferably used at from 80 to 120°F. The time for immersion in the plating solution can range from 1 to 30 minutes but is preferably from 1 to 5 minutes.

The immersion silver solution of the current invention is thus used to plate a thin layer of silver onto the surface to be soldered. It is believed that the resultant silver coating should be from 1 to 100 micro inches thick, preferably from 10 to 60 micro inches thick for effective enhancement and preservation of the solderability of the surface. Although this process is effective in

soldering many surfaces, it is particularly useful in soldering copper surfaces, such as Areas of Connection on printed circuit boards.

Although this technique may be utilized advantageously over almost any surface, it is most useful in the fabrication of printed circuit boards, particularly solder mask over bare copper (SMOBC) boards. Thus, in fabricating SMOBC boards, the solder mask is applied to the surfaces of the board then exposed and developed to reveal the Areas of Connection. These Areas of Connection are then essentially the only exposed areas of copper on the board, with the remainder essentially being covered by solder mask. These exposed Areas of Connection are thus destined to be points of attachment, in most cases by soldering, when the electronic components are later placed on the board later in the fabrication cycle. Therefore, the solderability of these exposed points, generally copper, must be enhanced and preserved.

Thus according to the current invention these areas are then preferably cleaned, using an acid cleaner, and subsequently microetched to prepare the surface for acceptable immersion plating. Following this preferred preparation, the board is immersed in the immersion silver plating solution, such that a silver deposit of appropriate thickness is achieved.

The invention is further described for illustrative purposes only in the following examples which are in no way limiting of the invention itself. In each of the examples standard IPC-B-25 test circuit boards are utilized in order to provide consistency. IPC-B-25 standard is incorporated herein by reference in its entirety.

Example I

IPC-B-25 test circuit boards were processed with the following steps:

a). Acid Cleaner, 5 minutes, 120°F

b). Water Rinse

c). Sodium persulfate/sulfuric acid microetch, 1 minute, 95°F

d). Water rinse

e). Water rinse

f). Immersion silver plate using the following composition

hydroxy ethylenediamine tetraacetic acid	10 gr/l
silver nitrate	2.4 gr/l
igepal Co730	5.0 gr/l
imidazole	10 gr/l
nitric acid	32.0 ml/l

g). water rinse.

The circuit boards were then tested according to the Bellcore GR-78-Core (13.2.5, 13.2.7) standard test method and the results are recorded in Table 1.

Example II

IPC-B-25 test circuit boards were treated as noted in Example 1 except that in this case the immersion silver plating bath also contained 5.0 gr/l of tallow amine ethoxylated with 15 moles

of ethylene oxide. The circuit boards were then tested according to the Belcore GR-78-Core (13.2.5, 13.2.7) standard test method and the results are recorded in Table 1.

Example III

IPC-B-25 test circuit boards were treated as noted in Example 1 except that in this case the immersion silver plating bath also contained 1.1 g/l of Pamak 25-S which is available from Hercules, Incorporated of Wilmington, Delaware and is a blend of fatty and resinous acids. The circuit boards were then tested according to Belcore GR-78-Core (13.2.5, 13.2.7) standard test method and the results are recorded in Table 1.

Example IV

IPC-B-25 test circuit boards were treated as noted in Example 1 except in this case after step (g) the circuit boards were further processed as follows:

h). treatment with an aqueous solution containing:

5.0 gr./l Cyastat L5 (quaternary ammonium methylsulfate of a fatty amidoalkyl amine)

32 ml/l Nitric Acid (70%)

balance - water.

i). water rinse.

The circuit boards were then tested according to Belcore GR-78-Core (13.2.5, 13.2.7) standard test method and the results are recorded in Table 1.

Example V

IPC-B-25 test circuit boards were treated as noted in Example IV except that in this case the Cyastat LS was replaced with 5.0 gr/l Cocoamine ethoxylated with 2 moles of ethylene oxide. The circuit boards were then tested according to Belcore GR-78-Core (13.2.5, 13.2.7) standard test method and the results are recorded in Table 1.

We Claim:

1. A process for improving the solderability of a metal surface, said process comprising treating the metal surface with an immersion silver plating solution, said solution comprising:

    a). a soluble source of silver ions;

    b). an acid;

    c). an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphoteric salts, resinous amines, resinous amides, fatty acids, resinous acids, ethoxylated versions of any of the foregoing, propoxylated versions of any of the foregoing and mixtures of any of the foregoing.

2. A process according to claim 1 wherein the silver plating solution also comprises material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives and benzimidazole derivatives.

3. A process according to claim 1 wherein the silver plating solution also comprises an oxidant.

4. A process according to claim 1 wherein the metal surface comprises copper.

5. A process according to claim 1 wherein the additive is selected from the group consisting of ethoxylated tallowamine, ethoxylated cocoamine, tallow amine, cocoamine, amines derived from tall oil acids, ethoxylated amines derived from tall oil acids, stearic acid, oleic acid, palmitic acid, acids derived from the distillation of tall oil, (stearamidopropyl)

dimethyl hydroxyethylammonium dihydrogen phosphate, alkyliminodipropionic acid monosodium salts, and mixtures of the foregoing.

6. A process according to claim 4 wherein the silver plating solution also comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

7. A process according to claim 6 wherein the silver plating solution also comprises an oxidant.

8. A process according to claim 7 wherein the additive is selected from the group consisting of ethoxylated tallowamine, ethoxylated cocoamine, tallow amine, cocoamine, amines derived from tall oil acids, ethoxylated amines derived from tall oil acids, stearic acid, oleic acid, palmitic acid, acids derived from the distillation of tall oil, (stearamidopropyl) dimethyl hydroxyethylaminium dihydrogen phosphate, alkyliminadipropionic acid monosodium salts, and mixtures of the foregoing.

9. A process for improving the solderability of a metal surface, said process comprising:

a). contacting the metal surface with an immersion silver plating solution thereby producing an immersion silver plate upon the metal surface; and thereafter

b). treating the immersion silver plated metal surface with a solution comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphateric salts, resinous amines, resinous amides, fatty acids, resinous acids, ethoxylated versions of any of the foregoing, and mixtures of any of the foregoing.

10. A process according to claim 9 wherein the silver plating solution comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives and benzimidazole derivatives.

11. A process according to claim 9 wherein the silver plating solution also comprises an oxidant.

12. A process according to claim 9 wherein the metal surface comprises copper.

13. A process according to claim 9 wherein the additive is selected from the group consisting of ethoxylated tallowamine, ethoxylated cocoamine, tallow amine, cocoamine, amines derived from tall oil acids, ethoxylated amines derived from tall oil acids, stearic acid, oleic acid, palmitic acid, acids derived from the distillation of tall oil, (stearamidopropyl) dimethyl hydroxyethylaminium dihydrogen phosphate, alkyliminadipropionic acid monosodium salts, and mixtures of the foregoing

14. A process according to claim 12 wherein the silver plating solution comprises a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

15. A process according to claim 14 wherein the silver plating solution also comprises an oxidant.

16. A process according to claim 15 wherein the additive is selected from the group consisting of ethoxylated tallowamine, ethoxylated cocoamine, tallow amine, cocoamine, amines derived from tall oil acids, ethoxylated amines derived from tall oil acids, stearic acid, oleic acid, palmitic acid, acids derived from the distillation of tall oil,

(stearamidopropyl) dimethyl hydroxyethylaminium dihydrogen phosphate, alkyliminadipropionic acid monosodium salts, and mixtures of the foregoing.

17. An immersion silver plating solution comprising an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphateric sales, resinous amines, resinous amides, fatty acids, resinous acids, ethoxylated versions of any of the foregoing, and mixtures of any of the foregoing.

18. An immersion plating solution according to claim 17 also comprising a material selected from the group consisting of imidazoles, benzimidazoles, imidazole derivatives, and benzimidazole derivatives.

19. An immersion plating solution according to claim 17 also comprising an oxidant.

20. An immersion plating solution according to claim 17 wherein the additive is selected from the group consisting of ethoxylated tallowamine, ethoxylated cocoamine, amines derived from tall oil acids, ethoxylated amines derived from tall oil acids, stearic acid, oleic acid, palmitic acid, acids derived from the distillation of tall oil, (stearamidopropyl) dimethyl hydroxyethylaminium dihydrogen phosphate, alkyliminadipropionic acid monosodium salts, and mixtures of the foregoing.

Method for Enhancing the Solderability of a Surface

Abstract of Disclosure

A method for enhancing the solderability of a metallic surface is disclosed where the metallic surface is plated with an immersion silver plate prior to soldering, which immersion silver plate is treated with an additive selected from the group consisting of fatty amines, fatty amides, quaternary salts, amphateric salts, resinous amines, resinous amides, fatty acids, resinous acids, ethoxylated derivatives of any of the foregoing, and mixtures of any of the foregoing. The immersion silver deposits created are resistant to electromigration.

a:53.297-056

Docket No. 297-056

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method for Enhancing the Solderability of a Surface

the specification of which

(check one) ___X___ is attached hereto.

_____ was filed on _____ as

Application Serial No. _____

and was amended on _____
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. To the best of my knowledge, information and belief the facts stated therein are true.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, 199 of any foreign application (s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application (s)

None___ _____ _____ _____ _____

(Number) (Country) (Day/Month/Year Filed) Yes No

_____ _____ _____ _____ _____

(Number) (County) (Day/Month/Year Filed) Yes No

_____ _____ _____ _____ _____

(Number) (Country) (Day/Month/Year Filed) Yes No

I hereby claim the benefit under Title 35, United States Code, 120 of any United States Application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulation, 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

None _____ _____ _____
(Serial No.) (Country) (Status patented, pending, abandoned)

_____ _____ _____
(Serial No.) (Country) (Status patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint **John L. Cordani**,

Registration No. **37,297**, with full power of substitution, association and revocation, as attorney to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, with an associated power of attorney to
None

Registration No. _____.

Please direct all telephone calls to the first named attorney at telephone No. (203) 575-5646 and send all correspondence to him at **245 Freight Street Waterbury, CT. 06702.**

Full name of sole first inventor **Ronald Redline**

Inventor's signature Ronald Redline Feb 12, 1999
(Date)

Residence: **28 Platt Drive, Prospect, CT. 06712**

Citizenship: **United States**

Post Office Address: **28 Platt Drive, Prospect, CT. 06712**

Full name of second joint inventor, if any **David Sawoska**

Inventor's signature ______________________ Feb. 12, 1999
(date)

Residence: **22 Kent Terrace, Watertown, CT.**

Citizenship: United States

Post Office Address: **22 Kent Terrace, Watertown, CT.**

Full name of third joint inventor, if any **Peter Kukanskis**

Inventor's signature ______________________ Feb. 12, 1999
(date)

Residence: **245 Quassapaug Road, Woodbury, CT.**

Citizenship: P.K. United States

Post office address: **245 Quassapaug Road, Woodbury, CT.**

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